7.   VOLATILE ORGANIC COMPOUND MEASUREMENTS

Title I, Section 182, of the Clean Air Act Amendments of 1990 required the Environmental Protection Agency to revise exisiting current ambient air quality surveillance regulations. The rule required States with areas classified as serious, severe, or extreme for ozone nonattainment to establish enhanced ambient air monitoring stations called Photochemical Assessment Monitoring Stations (PAMS) as part of their State Implementation Plan (SIP) (Federal Register, 1993).   Each station measures speciated hydrocarbons and carbonyl compounds, ozone, oxides of nitrogen, and surface meteorological data. Provisions of the rules require the operation of up to five PAMS stations in each nonattainment area depending on population.   Additionally, each area must monitor upper air meteorology at one representative site. In California, PAMS is required in Ventura County, and the South Coast, Southeast Desert and San Diego air basins. The program began in 1994, and is being phased-in over a five year schedule at a rate of at least one station per area per year.

The plan for measurements of volatile organic compounds (VOC) for the SCOS97-NARSTO program is built upon the foundation provided by the PAMS networks in the study region. PAMS ozone precursor monitoring is conducted annually in California during the peak ozone season (July 1 to September 30).   As is shown in Table 1-1, there will be 13 PAMS in operation during SCOS97-NARSTO (three in Ventura County; five in the South Coast Air Basin, one in the Southeast Desert Air Basin, and four in the San Diego Air Basin). Four 3-hour samples are collected every third day during the monitoring period at all PAMS sites for speciated hydrocarbon and at Type 2 sites only for carbonyl compounds. In addition to the regularly scheduled measurements, samples are collected on a forecast basis during five high-ozone episodes of at least two consecutive days. Episodic measurements consist of four samples per day for speciated hydrocarbon at all PAMS sites and for carbonyl compounds at Type 2 sites. Ventura County Air Pollution Control District and the San Diego Air Pollution Control District will supplement their existing sampling schedule to include all SCOS97 IOP days. Field operators from the University of California, Riverside College of Engineering – Center for Environmental Research and Technology (CE-CERT) will collect VOC samples in the SoCAB during SCOS97 IOPs. Airborne VOC samples will also be collected onboard the four instrumented aircrafts that will be deployed during the study.   These samples will be analyzed at Biospheric Research Corporation (BRC) for hydrocarbon and at Atmospheric Assessment Associates, Inc. (AtmAA) for carbonyl compounds.   VOC samples will also be collected in Mexicali and Tijuana, Mexico and analyzed at the Desert Research Institute (DRI).

Intended applications for the PAMS database include ozone and precursor trends, emission inventory reconciliation and verification, population exposure analyses, photochemical modeling support, and control strategy evaluation. The overlapping objectives and air quality and meteorological data requirements for PAMS and SCOS97-NARSTO provide an opportunity to address the quality assurance and data validation need of both programs, and to evaluate PAMS with respect to EPA's stated goals and objectives.

7.1 Sampling Site Selection Criteria

Design criteria for the PAMS network are based on selection of an array of site locations relative to ozone precursor source areas and predominant wind directions associated with high ozone events. Specific monitoring objectives are to characterize precursor emission sources within the area, transport of ozone and its precursors into and out of the area, and the photochemical processes related to ozone nonattainment, as well as developing an initial urban toxic pollutant database. A maximum of five PAMS sites are required in affected nonattainment areas, depending on the population of the Metropolitan Statistical Area/Consolidated Metropolitan Statistical Area (MSA/CMSA) or nonattainment area, whichever is larger. Specific monitoring objectives associated with each of these sites result in four distinct site types.

Type 1 sites are established to characterize upwind background and transported ozone and its precursor concentrations entering the area and to identify those areas which are subjected to overwhelming transport. Type 1 sites are located in the predominant morning upwind direction from the local area of maximum precursor emissions during the ozone season. Typically, Type 1 sites will be located near the edge of the photochemical grid model domain in the predominant upwind direction from the city limits or fringe of the urbanized area.

Type 2 sites are established to monitor the magnitude and type of precursor emissions in the area where maximum precursor emissions are expected. These sites also are suited for the monitoring of urban air toxic pollutants. Type 2 sites are located immediately downwind of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district. Additionally, a second Type 2 site may be required depending on the size of the area, and will be placed in the second-most predominant morning wind direction.

Type 3 sites are intended to monitor maximum ozone concentrations occurring downwind from the area of maximum precursor emissions. Typically, Type 3 sites will be located 10 to 30 miles downwind from the fringe of the urban area.

Type 4 sites are established to characterize the extreme downwind transported ozone and its precursor concentrations exiting the area and identify those areas which are potentially contributing to overwhelming transport in other areas. Type 4 sites are located in the predominant afternoon downwind direction, as determined for the Type 3 site, from the local area of maximum precursor emissions during the ozone season. Typically, Type 4 sites are located near the downwind edge of the photochemical grid model domain.

7.2 Installation

Sampling equipment are installed in available buildings in temperature-controlled environments with sample inlet systems and manifolds, air conditioning, and power distribution.

7.3 Sampling Site Locations

The current status of the implementation of PAMS by local air pollution control districts in southern California is outlined in Table 1-1. Thirteen PAMS sites will be operational by 1997 (three in Ventura County; five in the South Coast Air Basin, one in the Southeast Desert Air

Basin, and four in the San Diego Air Basin). Supplemental VOC samples will be collected by CE-CERT at San Clemente, Azusa, Los Angeles – North Main, and Burbank. VOC samples will also be collected at Mexicali and Tijuana, Mexico to characterize the southern boundary of the SCOS97-NARTSO study domain.

## 7.4	Measurement Methods and Procedures

EPA methods TO-14 and TO-11 are specified by the EPA for sampling and analysis of speciated hydrocarbons and carbonyl compounds, respectively (EPA, 1991). Table 7-1 lists the species that are currently in the DRI calibration table and PAMS target hydrocarbon species. For carbonyl compounds, state and local agencies are currently required to report only formaldehyde, acetaldehyde and acetone. The districts may be able to quantify and report several C_3 to C_7 carbonyl compounds that appear in the HPLC chromatograms. The EPA rule requires eight 3-hour hydrocarbon samples (midnight-3 am, 3-6 am, 6-9 am, 9-noon, noon-3 pm, 3-6 pm, 6-9 pm, and 9-midnight PDT) every day at Type 2 sites and every third day at all other PAMS sites. Sampling for carbonyl compounds is required at Type 2 sites only. In addition, one 24-hour sample is required every sixth day year-round at Type 2 sites and during the summer monitoring period at all other sites. Under the California Alternative Plan, four 3-hour samples (3-6 am, 6-9 am, 1-4 pm, and 5-8 pm, PDT) are collected every third day during the monitoring period at all PAMS sites for speciated hydrocarbons and at Type 2 sites only for carbonyl compounds. In addition to the regularly scheduled measurements, samples are collected on a forecast basis during up to five high-ozone episodes of at least two consecutive days. Episodic measurements consist of four samples per day (6-9 am, 9-noon, 1-4 pm and 5-8 pm, PDT) for speciated hydrocarbons at all PAMS sites and for carbonyl compounds at Type 2 sites. The VCAPCD and SDAPCD operate their PAMS sites according to the alternative plan, while SCAQMD operates theirs according to the EPA Rule. SCAQMD's 3- hour sampling schedule (on PST year round) begins one hour later than sampling times used by VCAPCD and SDAPCD (on PDT for PAMS). The PAMS 3-hour VOC sampling schedule should be consistent throughout the SCOS97 study area.

Total nonmethane hydrocarbon (NMHC) concentrations are monitored at some PAMS sites by automated-Preconcentration Direct Injection Flame Ionization Detection (PDFID) (e.g., Xontech 850). Total NMHC is measured by passing the air sample through a chromatographic column to separate methane from other hydrocarbons and analyzing the bulk hydrocarbon sample by FID. In the FID, sample air is burned in a hydrogen flame creating a quantity of ions from the hydrogen molecules in the air sample. The ions conduct a small electrical current which is measured by an electrometer, which in turn produces an electronic signal proportional to the number of ions collected. Thus, the total hydrocarbon data are reported as parts per billion carbon (ppbC).

### 7.4.1	Hydrocarbons Sampling and Analysis Methods (Biospheric Research Corporation)

Whole-air samples for hydrocarbon analysis are collected in passivated stainless steel canisters with the aid of a pump regulated to achieve a final canister pressure above atmospheric pressure. The flow rate and sample duration are matched in order to maintain constant flow

Table 7-1

DRI Laboratory Calibration Species

Retention Time	Retention Index	Name	PAMS Compound
Quantitated from GS-A column:			
		ethene	p
		acetylene	p
		ethane	p
		propene	p
		propane	p
		1-butene	p
		iso-butene	
Quantitated from DB-1 column:			
3.85		C2 compounds	
6.84		propene	p
7.10	300.00	propane	p
8.55	316.39	freon 12	
10.87	361.34	iso-butane	p
12.41	389.71	1-butene+iso-butene	p
12.67	393.91	1,3-butadiene	
12.94	400.00	n-butane	p
13.15	404.08	methanol	
13.62	411.32	t-2-butene	p
14.03	418.74	1&2-butyne	
14.43	426.16	c-2-butene	p
16.18	456.77	3-methyl-1-butene	
16.44	461.60	ethanol	
16.88	470.87	acetonitrile	
17.12	474.21	isopentane	p
17.27	476.99	acetone	
17.95	489.24	1-pentene	p
18.31	495.92	2-methyl-1-butene	
18.53	500.00	n-pentane	p
18.75	504.44	isoprene	p
18.97	508.67	t-2-pentene	p
19.35	516.33	c-2-pentene	p
19.59	520.77	2-methyl-2-butene	p
20.21	532.86	Freon 113	
20.30	535.08	2,2-dimethyl-butane	p
20.72	543.55	2-methylpropanal	
21.11	552.02	cyclopentene	
21.24	554.64	methacrolein	
21.35	556.85	4-methyl-1-pentene	
21.62	562.30	cyclopentane	p
21.78	565.32	2,3-dimethylbutane	p

Table 7-1

DRI Laboratory Calibration Species

Retention Time	Retention Index	Name	PAMS Compound
21.85	566.90	MTBE	
22.02	569.96	2-methylpentane	p
22.16	572.98	butanal	
22.41	578.02	butanone	
22.68	583.47	3-methylpentane	p
22.92	588.31	2-methyl-1-pentene	p
22.99	589.31	1-hexene	
23.18	593.95	C6 Olefin	
23.51	600.00	n-hexane	p
23.57	601.34	chloroform	
23.63	602.68	t-3-hexene	
23.72	604.70	c-3-hexene	
23.84	607.38	t-2-hexene	
23.97	610.29	2-methyl-2-pentene	
24.15	614.32	c-2-hexene	
22.40	620.58	3-methyl-2-pentene	
22.59	624.83	2,2-dimethylpentane	
24.69	627.07	methylcyclopentane	p
24.89	631.32	2,4-dimethylpentane	p
25.09	635.35	mechloroform	
25.35	641.61	2,2,3-trimethylbutane	
25.61	647.43	1-methylcyclopentene	
25.77	651.01	benzene	p
25.99	655.93	3,3-dimethylpentane	
26.18	660.85	cyclohexane	p
26.37	665.10	4-methylhexene	
26.54	668.46	2-methylhexane	p
26.63	670.69	2,3-dimethylpentane	p
26.78	674.05	cyclohexene	
26.92	677.18	3-methylhexane	p
27.02	680.31	C7 Olefin	
27.20	684.34	1,3-dimethylcyclopentane	
27.35	687.02	3-ethylpentane	
27.51	690.60	2,2,4-trimethylpentane	p
27.70	694.85	C7 Olefin	
27.83	697.76	t-3-heptene	
27.94	700.00	n-heptane	p
28.08	704.46	C8 Olefin	
28.18	706.93	C8 Olefin	
28.31	709.90	C8 Olefin	
28.43	712.13	2,4,4-trimethyl-1-pentene	
28.89	724.75	methylcyclohexane	p

Table 7-1

DRI Laboratory Calibration Species

Retention Time	Retention Index	Name	PAMS Compound
29.06	728.96	C8 Paraffin	
29.24	733.42	2,5-dimethylhexane	
29.34	735.89	2,4-dimethylhexane	
29.69	743.81	C8 Paraffin	
30.08	753.47	2,3,4-trimethylpentane	p
30.28	758.66	toluene	p
30.45	762.87	2,3-dimethylhexane	
30.65	767.33	2-methylheptane	p
30.73	769.31	4-methylheptane	
30.86	772.52	C8 Paraffin	
30.96	775.25	3-methylheptane	p
31.08	778.22	hexanal	
31.31	783.91	2,2,5-trimethylhexane	
31.40	786.14	1-octene	
31.51	788.86	1,1-dimethylcyclohexane	
31.96	800.00	n-octane	p
32.67	819.29	2,3,5-trimethylhexane	
32.80	822.83	2,4-dimethylheptane	
32.90	825.54	4,4-dimethylheptane	
33.13	831.79	2,6-dimethylheptane	
33.38	838.59	2,5-dimethylheptane	
33.58	844.29	3,3-dimethylheptane	
33.68	847.01	C9 Olefin	
32.87	852.17	C9 Olefin	
33.98	855.16	ethylbenzene	p
34.15	859.78	C9 Olefin	
34.28	863.59	m&p-xylene	p
34.45	868.38	2-methyloctane	
34.66	873.91	3-methyloctane	
34.84	878.80	C9 Paraffin	
34.95	881.79	styrene	p
35.15	887.23	o-xylene	p
35.40	894.02	1-nonene	
35.52	897.28	C9 Paraffin	
35.61	900.00	n-nonane	p
35.73	903.55	C9 Paraffin	
35.89	908.28	C9 Olefin	
36.39	914.79	C9 Paraffin	
36.56	926.04	isopropylbenzene	p
36.84	928.11	isopropylcyclohexane	
36.67	932.83	alpha-pinene	
36.86	937.28	benzaldehyde	

Table 7-1

DRI Laboratory Calibration Species

Retention Time	Retention Index	Name	PAMS Compound
36.98	940.83	2,6-dimethyloctane	
37.08	943.79	C10 Olefin	
37.18	946.75	3,6-dimethyloctane	
37.31	950.59	n-propylbenzene	p
37.54	957.40	m-ethyltoluene	p
37.62	959.76	p-ethyltoluene	p
37.79	964.79	1,3,5-trimethylbenzene	p
37.92	968.64	C10 Paraffin	
38.08	973.27	beta-pinene	
38.19	976.63	o-ethyltoluene	p
38.41	983.14	C10 Paraffin	
38.68	991.42	1,2,4-trimethylbenzene	p
38.97	1000.00	n-decane	p
39.08	1003.51	C10 Aromatic	
39.30	1010.54	isobutylbenzene	
39.53	1017.89	C10 Olefin	
39.66	1022.04	1,2,3-trimethylbenzene	p
39.78	1025.88	C10 Paraffin	
39.94	1030.99	indan	
40.12	1036.74	indene	
40.32	1043.13	m-diethylbenzene	p
40.42	1046.33	C10 Aromatic	
40.50	1048.88	p-diethylbenzene	p
40.68	1054.63	n-butylbenzene	
40.88	1061.02	o-diethylbenzene	p
41.08	1067.41	C10 Aromatic	
41.34	1075.72	1,3-dimethyl-4-ethylbenzene	
41.42	1078.27	C10 Aromatic	
41.60	1084.03	isopropyltoluene	
42.07	1100.00	n-undecane	p
42.27	1106.90	C10 Aromatic	
42.50	1114.83	C11 Paraffin	
42.62	1118.97	1,2,4,5-tetramethylbenzene	
43.13	1122.76	1,2,3,5-tetramethylbenzene	
43.38	1131.38	C11 Paraffin	
43.75	1144.14	2-methylindan	
44.15	1157.93	1-methylindan	
44.27	1162.07	C11 Aromatic	
44.36	1179.66	C11 Aromatic	
44.72	1192.07	naphthalene	
44.95	1200.00	n-dodecane	

during the sampling period. Prior to sample collection, the canisters are evacuated to less than 0.1 torr vacuum, and placed in a 125 °C oven for three hours. A fraction of the cleaned canisters were filled with zero air and analyzed by TO-12. The batch acceptance criteria for the canisters is less than 0.2 ppbC per hydrocarbon peak.

The C_2 and C_3 hydrocarbons are analyzed by BRC using a Hewlett Packard 5790 gas chromatograph with an FID detector. Sample aliquots are loaded onto a glass bead freezeout loop immersed in liquid oxygen. The components are desorbed from the cryofocus loop, and separated using a packed column of phenylisocyanate/Porasil C at 45 °C. The C_4 and C_{10} hydrocarbons are analyzed by OGI using a Hewlett Packard 5890A gas chromatograph with FID detector. Sample aliquots of 500 ml are loaded onto a 1/8 inch by 6 inch glass bead freezeout loop immersed in liquid oxygen. The components are desorbed with 90 °C hot water onto a capillary cryofocus loop at the head of the column at -60 °C. They are then desorbed from the cryofocus loop, and separated using a 60-meter 0.25-micron J&W Scientific DB-1 capillary column with a 1.0-micron coating. The column is programmed from –60 °C to 200 °C at 4 °C/min. The chromatograms are integrated using the HP ChemStation computer data station and stored onto a hard disk. Data from the integrator are entered into a spreadsheet to generate the final report. The detection limits for this method are 0.1 ppbC for the hydrocarbon target compounds and the precision of the analysis at 5 ppbC is 10 percent.

The calibration by BRC is in terms of mass (area response/ng) of neohexane, which is used as an internal standard in each sample. The neohexane is traced to NIST benzene SRM (0.254 ppmv). For comparative purposes, OGI converts their hydrocarbon concentrations from $\mu g/m^3$ units to ppbC. A problem exists in selecting the most suitable conversion factor(s). The factors that convert mixing ratios in ppbC to mass concentration in $\mu g/m^3$ will vary among hydrocarbons because the molecular weight/number of carbon atoms ratios are not constant for all hydrocarbons. At 1 atm pressure and 25 °C, the ($\mu g/m^3$) to ppbC conversion factor for methane is 1.5 and 1.88 for benzene. The conversion factor for propane (1.67) is selected OGI. If conversion factors specific to each hydrocarbon are employed instead, the corresponding concentrations will be up to 5 percent higher for alkane, 5 to 10 percent higher for alkenes and cycloalkane, and 10 to 15 percent higher for aromatic hydrocarbons.

BRC recently participated in a hydrocarbon audit and laboratory comparison as part of the NARSTO-Northeast Study. The other participants were the State University of New York at Albany (SUNYA), EPA Region I, and eight of the Photochemical Assessment Monitoring Station (PAMS) networks in the northeastern U.S. (Maine, Connecticut, Massachusetts, Maryland, City of Philadelphia, New Jersey, New York, and Virginia). The Desert Research Institute (DRI), which conducted measurements in roadway tunnels in New York and Boston during the summer of 1995 also participated in the performance audits. The results were evaluated and reported by Fujita et al. (1996). The hydrocarbon measurement comparison consisted of two synthetic samples used by the Environmental Protection Agency in the Photochemical Assessment Monitoring Station (PAMS) program, and two ambient samples collected by EPA in the Research Triangle Park area. The samples were analyzed by the contracting laboratory and by the Environmental Protection Agency Atmospheric Research and Exposure Assessment Laboratory, which served as the referee laboratory. The main findings of the audit listed below.

- In general, the values reported by the audited laboratories were well correlated with the values obtained by EPA. Eight of the twelve, including both BRC and DRI, reported values that were within 10 percent of EPA for all four audit samples. Mean values greater than 1.0 ppbC with Laboratory/EPA ratio greater than 0.7 and less than 1.3 were used for the calibration checks in order to minimize the effect of inconsistent identifications on the correlations.

- Because calibration differences are generally within 10 percent, the outliers (i.e., data pairs with mean concentrations greater than 1.0 ppbC with Laboratory/EPA ratio less than 0.7 and greater than 1.3) are likely due to differences in peak identification between the audited laboratory and EPA. The ratios of outliers to number of compounds in the sample with concentrations greater than 1 ppbC indicate the degree of inconsistency in peak identification. The average of the ratios of outliers for the four audit samples are less than 10 percent for four of the groups (including DRI), 10 to 20 percent for five of the groups (including BRC), and 20 to 30 percent for three of the groups.

- The sum of the PAMS target compounds and total NMHC in the PAMS region of the chromatogram reported by the audited laboratories were generally within 10 percent of the corresponding EPA values.

- Examination of the other subtotals reported by EPA provided an indication of the relative importance of organic compounds that are not PAMS target compounds. For the ambient samples used in the audit, which reflect mostly motor vehicle emissions, sums of identified compounds that are not PAMS target compounds are 10 to 25 percent of the total NMHC (up to n-undecane). Semi-volatile hydrocarbons beyond n-undecane that can be measured from canisters are equivalent to 4-9 percent of the total NMHC up to undecane. Concentrations of oxygenated compounds, mainly methanol, were variable and were probably artifacts that were introduced when the samples were diluted by EPA. Oxygenated compounds typically represent a larger fraction of total NMOC in receptor area.

- Without exception, all of the species in the synthetic mixtures, once in the transfer canisters, were stable (within 5 percent of the original values) throughout the duration of the comparison study (up to three months). Initial and repeat values for most species were also within 5 to 10 percent of the NIST-traceable values. These results provide confirmation of the accuracy of EPA's analyses. Several unstable and higher-molecular weight species showed decreases from their reference values. Acetylene and 2-methyl-1-pentene values were less than 50 percent of the reference value. Styrene, n-propylbenzene, m- and p-diethylbenzene were less than 80 percent, and p- and o-ethyltoluene and n-undecane were less than 90 percent of the reference values. However, even these species remained stable for up to three months once the dry synthetic mixtures were transferred to a humidified canister.

7.1.2   Sampling and Analysis Methods for Carbonyl Compounds (AtmAA)

The technique used by AtmAA to measure ambient carbonyl compounds is an established procedure using C_{18} (octadecylsilane-bonded silica) Sep-Pak cartridges (Waters Associates, Milford, MA) which have been impregnated with purified acidified 2,4-dinitrophenylhydrazine

(DNPH). When ambient air is drawn through the cartridge, carbonyls in the air sample react with DNPH to form hydrazones, which are separated and quantified using HPLC in the laboratory (Fung and Grosjean 1981). This technique is the most commonly used method for measuring these compounds in ambient air.   The variation of this methods used in the PAMS program replaces the C_{18} substrate with DNPH-coated silica gel Sep-Pak cartridges and an upstream KI scrubber to remove ozone, which causes a negative interference with the method.

Cartridge samples are taken using an automated sampler with six channels to collect samples sequentially on an event basis. The sampler has a seventh channel for taking either a duplicate sample concurrently with one of the active channels, or a field blank. Since cartridges will naturally sorb carbonyl compounds from the surrounding air if left open, the sampler has been designed such that cartridges loaded into the sampler are isolated from the environment and from each other by check valves upstream and solenoid valves downstream. Memory protected programmable timers are used to control the operation of the pump and the solenoid valves according to the prescribed schedule. Duplicate samples can be collected on collocated cartridges by activating a parallel channel simultaneously. A mode selection switch converts the parallel channel for field blank collection as well. Sampling flow rates are controlled at ∼0.9 liter/min using a differential flow controller with a typical precision of ± 5% or less.

The samples are analyzed in batches of 20 to 40 cartridges. Each cartridge is eluted with 3 ml of acetonitrile into a graduated polyethylene tube with a resealable cap. The exact volume is calibrated gravimetrically. An aliquot of the eluent is transferred into a 2-ml septum vial and injected with an autosampler into a high performance liquid chromatograph (Shimadzu LC-6) for separation and quantitation of the hydrazones. The samples are analyzed for formaldehyde, acetaldehyde, acetone, propanal, benzaldehyde, o-tolualdehyde, and C_4 to C_6 aliphatic carbonyls group by carbon number.

Derivation of carbonyl compounds by 2,4-dinitrodinitrophenylhydrazine (DNPH) followed by liquid chromatography and u.v. detection is currently the most widely used method for measurement of ambient carbonyl compounds. Two variations of this methods will be used during SCOS97-NARSTO. AtmAA and DRI both collected ambient carbonyl compounds using C18 Sep-Pak cartridges impregnated with acidified DNPH reagent while local air pollution agencies in the study area used similarly impregnated silica Sep-Pak cartridges recommended by EPA Compendium Method TO-11, which is the standard method used nationally at Photochemical Assessment Monitoring Stations (PAMS). The PAMS variant of the of the DNPH method includes an ozone scrubber upstream of the impregnated cartridge since silica cartridges were found to have significant negative ozone artifacts. Despite the acceptance and widespread use of the DNPH methods, questions still remain regarding interferences and sampling artifacts associated with the methods.

The questions regarding the accuracy of the DNPH method is mainly concerned with sampling.   In order to address these questions, AtmAA participated in two measurement comparisons as part of an external quality assessment of carbonyl measurements for NARSTO-Northeast.   Results of AtmAA's comparisons with the Massachusetts Department of Environmental Protection at Agawam, MA, and with ManTech during the 1995 Nashville/Middle Tennessee Ozone Study are summarized by Fujita et al., (1996). The factors affecting carbonyl measurements by the DNPH method were review from published articles and discussion with

investigators active in this area in order to provide a perspective for interpreting the results from the two comparison studies. Relevant parameters include the substrate (type, DNPH loadings, blank levels, and variability), sampling conditions (ambient ozone concentrations, temperature, relative humidity, sample volume measurements, breakthrough, type of sampling line and ozone scrubber), sample storage, and handling (exposure to light and heat, type of storage and duration of storage), sample preparation and analysis.

- Reagent Loading and Blank Levels. Blank levels are related to the loading level of DNPH on cartridges in that higher loading levels almost always lead to higher blank levels. The formaldehyde average blank level for the Waters DNPH-coated ready-to-use silica Sep-Pak cartridges, which have a typical loading of 5 μmol of DNPH per cartridge (1 mg/cartridge) is 1.18 nmol/cartridge. The average formaldehyde blank level for C18 cartridges prepared by AtmAA, which have DNPH loadings of 10 μmol/cartridge (2 mg/cartridge), is 2.38 ± 0.51 nmol/cartridge. While the absolute blank level for the C18 cartridges is a factor of two higher than the silica gel cartridges, the relative standard deviation is in the same range as that found for commercial silica gel cartridges.

- Reagent pH. The rate and extent of reactions of DNPH with carbonyl compounds is pH dependent and vary with the compound.

- Relative Humidity. Decrease in collection efficiency of carbonyl compounds on C18 cartridges have been observed in dry air (RH = 3-7%) for ketones but not for aldehydes. The decrease in collection efficiency due to change in relative humidity should only be of concern in a limited number of applications since DNPH-coated cartridge measurements of carbonyls are seldom made in very dry air.

- Breakthrough. During the NARSTO-Northeast 1995 Ozone Study, 48 tandem C18 cartridges were collected to assess breakthrough in ambient samples. Except for acetone, all species up to C6 carbonyls average 95% efficiency or greater. Acetone collection efficiency averaged approximately 79%, with most of the lower values (45 to 65%) corresponding to the nighttime period when 6-hour samples were collected rather than 3 hour samples during the daylight hours. Average collection efficiency for acetone during daytime periods was over 90%.

- Ozone Artifacts A number of studies have reported (Arnts and Tejada, 1989) that DNPH-coated silica gel cartridges show a dramatic negative interference by ozone in the determination of formaldehyde. Most of these studies have observed no interference for formaldehyde with C18 substrates. The negative artifact arises from the reaction of ozone with the DNPH derivative. In the case of C18 cartridges, the radicals generated by the ozone attack can be scavenged by the C18 phase, thus limiting further attack on DNPH or hydrazone. With the C18 cartridge, a positive ozone interference was detected with the formation of a peak which coelutes with the HCHO hydrazone. Several chromatographic conditions were used without success to separate the coeluting peak, which suggests the possibility that the artifact is the HCHO hydrazone itself. The magnitude of the interference is approximately 1.7% of the number of moles of ozone that pass through the cartridge. The presence of ozone in the system does not lead to formation of peaks which are coincident to the hydrazones for the acetaldehyde or propionaldehyde. Artifacts reported have been on the cartridges prepared by individual researchers, and the cartridge

composition were not addressed in each case. The artifacts observed may not have been attributed solely to the substrate. Multiple factors, such as, among others, reagent formulation, loading, and acidity of the DNPH, are important in determining the extent of the artifacts that may occur. An experiment in which atmospheric samples were collected by collocated C18 and silica gel cartridges that were prepared by AtmAA at the same time under identical conditions gave comparable formaldehyde levels which also compared well to the TDLAS measurements. These results suggest that the type of substrate (C_{18} versus silica gel) is less critical than how the cartridge is prepared.

- <u>Comparison of the DNPH Method with Spectroscopic Measurements</u> Previous studies in California prior to and during the Southern California Air Quality Study (SCAQS) indicated that formaldehyde concentrations determined using C18 DNPH cartridges similar to those used in NARSTO-Northeast and planned for SCOS97-NARSTO compare well to those from continuous instruments such as long-path FTIR, DOAS, and TDLAS. Measurements of formaldehyde by C18 DNPH cartridges during SCAQS generally tracked ozone concentrations and were in reasonably good agreement with TDLAS measurements.   In contrast, SCAQS measurements of HCHO by silica gel DNPH cartridges were substantially lower in comparison to the TDLAS during the middle of the day, when ozone reached maximum concentrations. Similar results were also obtained during the 1993 Los Angeles Atmospheric Free Radical Experiment and in the NCAR/SOS Formaldehyde Intercomparison Study in Boulder.

- <u>Ozone Removal</u> For relative humidity less than approximately 5%, packed-KI scrubbers have extremely low capacity for ozone removal and breakthrough occurs within a few minutes at a flow of 1 L min^{-1} . Scrubbing efficiency increases substantially even at low levels of relative humidies (ca. 10%). In contrast, KI-coated copper tube denuders show negligible breakthrough even under dry conditions. At moderate to high RH, the ozone denuders have high capacity for ozone removal. Results show an efficiency of at least 24,000 ppbv-h for these devices. For an average ozone concentration (day and night) of 60 ppbv the devices are expected to be effective for at least 16 days when used at a flow rate of 1 L min^{-1}.   Carbonyl compounds are generally quite soluble in water and KI is a highly hygroscopic chemical. In test conducted at RH of 75%, there is no evidence of formaldehyde retention on KI scrubbers over typical sampling times. Other carbonyls have not been tested, and it is possible that carbonyl compounds with carbon number higher than C4 might be retained by the scrubber or denuder in some cases. Method TO-11 specifies heating the KI denuders to approximately 50 $^{\circ}$C to avoid formaldehyde loss.

- <u>Sample Handling and Storage</u> The amount of exposure is reduced significantly by using a protective closure compared to an open cartridge. For formaldehyde, a polyethylene cap provides about ten times more protection than PVC caps and about twice as much protection as plugs. Screw-capped vials offer additional protection. Hydrazones of stable carbonyls, such as formaldehyde, acetaldehyde, and acetone maintain their integrity on silica gel and C_{18} cartridges for over a month under refrigerated storage. However, the olefinic aldehydes such as acrolein and crotonaldehyde degrade partially on the cartridges, either during sampling or storage, and form unknown products. Exposure to sunlight

causes significant production of carbonyls which can be eliminated by wrapping the cartridges in aluminum foil during sampling and storage.

- <u>Lower Quantifiable Limits and Measurement Precision</u> Factors that may cause a bias in this measurement, such as breakthrough, blank variability, hydrazone product stability were evaluated and conducted as part of the QA/QC activities in NARSTO-Northeast. Based on field blanks and their variability, lower quantifiable limits (LQL) for 3-hour samples were approximately 0.4 ppbv or less for all but the >C6 carbonyls, which was estimated at 1 ppbv. The LQLs for 6-hour samples are half those values. Analytical precisions derived from repeat analysis range from 0.014 µg for propanal to 0.16 µg for >C6 carbonyls, corresponding to a coefficient of variation of 3 to 4% for the major components such as formaldehyde, acetaldehyde, and acetone. There were 26 pairs of collocated samples, which provided an estimation of the carbonyl measurement precision. Most species had a CV of 4 to 8%, except propanal (10.6%), C5 carbonyls (9%), and >C6 carbonyls (15.0%).

In summary, there are few measurement techniques which can be used to evaluate the accuracy of the carbonyl species concentrations made by the DNPH method. Previous studies in California prior to and during the Southern California Air Quality Study (SCAQS) indicated that formaldehyde concentrations determined using C_{18} DNPH cartridges similar to those used in NARSTO-Northeast compare well to those from continuous instruments such as long-path FTIR, DOAS, and TDLAS. There was a small negative bias of 0.7 ppb, corresponding to -6.9% at the mean formaldehyde concentration (10.2 ppb) observed during the study (Fung and Wright 1990, Lawson et al 1990). The average peak ozone concentration for the ten day study was approximately 195 ppb (Lawson et al 1990). Measurements of HCHO by C_{18} DNPH cartridges during SCAQS generally tracked ozone concentrations and were in reasonably good agreement with TDLAS measurements. Also, the HCHO data showed good agreements between the C_{18} DNPH cartridge and the TDLAS in the 1993 Los Angeles Atmospheric Free Radical Experiment (Mackay, 1994) and in the NCAR/SOS Formaldehyde Intercomparison Study (Calvert et al., 1996).   In contrast, SCAQS measurements of HCHO by silica gel DNPH cartridges were substantially lower in comparison to the TDLAS during the middle of the day, when ozone reached maximum concentrations.   Arnts and Tejada (1989) reported a significant ozone interference associated with EPA Method TO-11 using DNPH-coated silica gel cartridges. They observed a significant reduction in the level of formaldehyde measured in the presence of ozone. In the same study, they also evaluated cartridges prepared with the C_{18} substrate, and observed no interference for formaldehyde from ozone at the 120 ppb level used in the experiment. Arnts and Tejada concluded that the ozonolysis of formaldehyde hydrazone is apparently substrate dependent (silica gel vs C_{18}).   These results were subsequently reproduced by Mantech (Kleindienst, 1994).

Positive ozone artifacts have also been reported (Rodler and Birks, 1994) on formation of HCHO, methyl vinyl ketone, and methacrolein from isoprene, and several higher carbonyls from the C_{18} substrate. The C_{18} artifact observed by Rodler and Birks (1994) is contrary to the field data collected from the studies cited above in which daily ozone levels of 260 to 280 ppb were observed. An experiment in which atmospheric samples were collected by collocated C_{18} and

silica gel cartridges that were prepared at the same time under identical conditions gave comparable formaldehyde levels which also compared well to the TDLAS measurements (Fung, 1993). These results suggest that the type of substrate (C_{18} versus silica gel) is less critical than how the cartridge is prepared. Artifacts reported have been on the cartridges prepared by individual researchers, and the cartridge composition were not addressed in each case. The artifacts observed may not have been attributed solely to the substrate. Multiple factors, such as, among others, reagent formulation, loading, and acidity of the DNPH, are important in determining the extent of the artifacts that may occur.

With the exception of nighttime acetone values, it is likely that nominal accuracy of the DNPH carbonyl data is better than 20 percent for measured carbonyl species with concentrations above 2 ppb.

7.1.3   Airborne Sampling of Hydrocarbons and Carbonyl Compounds

Hydrocarbon sampling onboard aircraft is essentially the same as on the surface. However, because of the longer sampling times required for the DNPH-cartridge method, ambient samples are first collected in Tedlar bags. The air samples are transferred from the bags to cartridges soon after the flight has ended. Other than the transfer bag, the sampling procedures are identical to the collection of surface samples.

7.1.4   Carbon Monoxide, Carbon Dioxide and Methane

Methane (CH_4), carbon monoxide (CO), and carbon dioxide (CO_2) are measured from the canister samples using GC/FID. Since the FID does not respond to CO and CO_2, these species are converted to methane by a methanator, positioned after the GC column but ahead of the FID. The methanator comprises a firebrick powder impregnated with nickel catalyst, through which a stream of hydrogen gas flows continuously at ~550 °C. For compound separation, a 20-foot x 1/8-inch inner-diameter (i.d.) column packed with a 60/80 mesh of Carboxen 1000 (Supelco) is used. This column provides sufficient separation between CH_4 and CO, without retaining CO_2. Five ml samples are injected using a constant-volume loop. The detection limit for both CO and CH_4 is ~20 ppbv, whereas for CO_2 it is ~3 ppmv. The precision is generally better than 10%.

7.1.5   Oxygenated Organic Compounds

Methyl t-butyl ether is quantified from canister samples, using the method of analysis for C_3-C_{11} hydrocarbons. The individual response factor is determined for MTBE and its concentration is reported in ppbv. It is particularly important to obtain good separation of the MTBE peak, which normally elutes just before 2-methylpentane and after 2,3-dimethylbutane.

7.1.6   Halogenated Hydrocarbons

Halogenated compounds can be also quantified from canister samples, with the same column as used for C_3-C_{11} hydrocarbons. However, electron capture detection is used rather than flame ionization due to the weaker and variable response of halogenated compounds on the FID. This method will be used by DGA to measure peroxyacetylnitrate (PAN) as well as perchloroethylene and methylchloroform at Azusa and Simi Valley. A minimum of three canister

samples from Azusa should also be analyzed by the Desert Research Institute with their semi-continuous halocarbon analyzer and compared to values reported by DGA.

7.5   Systems Audits

The quality assessment of SCOS97-NARSTO VOC data included system audits of the two main VOC laboratories (AtmAA for carbonyl compounds and BRC for hydrocarbons). These audits include review of operational and quality control procedures to assess whether they are adequate to assure valid data which meet the specified levels of accuracy and precision.   An on-site systems audit of AtmAA was conducted in 1995 by Dr. Eric Fujita. The results of this audit will be summarized in lieu of an audit for SCOS97-NARSTO.

An on-site systems audit of BRC was not performed by DRI during the 1995-96 NARSTO-Northeast study.   However, two separate systems audits were performed by DRI staff within the last ten years at Dr. Rasmussen's laboratory at Oregon Graduate Institute (OGI). The first audit in 1987 during the Southern California Air Quality Study, and the second audit in 1990 during the San Joaquin Valley Air Quality Study. While the standard operating procedure for hydrocarbon analysis at BRC has not changed during this time, seven years is sufficient time to warrant a new systems audit. An on-site systems audit will be conducted at BRC by Dr. Zielinska of the DRI in May, 1997.

7.6   Performance Audits

7.6.1   Hydrocarbons

The hydrocarbon performance audits will consist of two ambient samples. A draft protocol is included as Appendix C. Participating laboratories include ARB, EPA, BRC, DRI, SDAPCD, SCAQMD, VCAPCD, and BAAQMD.   Each participating laboratory will supply to ARB, Monitoring and Laboratory Division two cleaned, evacuated 6-liter canisters by April 25, 1997. EPA, ARB and DRI will supply two additional canisters (four in all). ARB will fill the two sets of canisters to 20-25 psi with ambient air from the Los Angeles area using a manifold sampling system supplied by the Desert Research Institute. One set of canisters will be collected in the morning (after 6:00 a.m. and before 9:00 a.m., PDT) in an area heavily influenced by mobile source emission. The other set will be collected in the afternoon (after 1:00 p.m. and before 4:00 p.m., PDT) in a downwind area with maximum ozone levels. Duplicate samples will be collected for EPA, ARB and DRI (total of eleven simultaneous canister samples at each site).   ARB will send the two (or four) ambient audit samples to each participating laboratory by May 6, 1997. Each laboratory will analyze the audit samples within five working days after receiving the audit canisters. EPA, ARB and DRI will reanalyze their samples after one and two months to monitor the stability of the audit samples. Analytical results will be compiled by the California Air Resources Board, Research Division and results will be summarized by DRI.

7.6.2   Carbonyl Compounds

The carbonyl performance audit will consist of sampling under field conditions with addition of a standard mixture of carbonyls from a 6-liter stainless steel canister to an ambient sample. A draft protocol is included in Appendix E. The can will also contain benzene for quality control purposes.

The main supply of the standard mixture will be prepared at the Desert Research Institute in a 33-liter tank. The standard mixture in a 6-liter canister and a dilution apparatus will be supplied by the Desert Research Institute, along with operating instructions. The standard audit protocol will consist of a 3-hour ambient sample using two DNPH cartridges in series (same as a breakthrough experiment) with addition of the standard mixture, with appropriate dilution, between the two cartridges. The front cartridge serves to scrub ambient carbonyl compounds and ozone. Each group will collect two samples and pass the 6-liter canister and gas dilution system on to the next group. The 6-liter canisters will hold sufficient sample for two groups. The Air Resources Board, Monitoring and Laboratory Division will analyze the contents of the canister by DNPH/HPLC prior to shipment and upon its return. The contents of the main tank will be periodically analyzed by both DNPH/HPLC and GC/FID (for higher MW carbonyls). These audits will be performed in June 1997.

A similar audit was conducted for the 1996 NARSTO-Northeast Study. The results of the audit are currently under review by the Dr. Eric Fujita of the DRI. Preliminary results indicate that formaldehyde, acetaldehyde and acetone are stable in both the main tank and in the 6-liter transfer canisters. Two higher aldehyde, pentanal and benzaldehyde, while stable in the 33-liter canister under high pressure (60-80 psi), show significant loss in the 6-liter transfer canisters (10-25 psi).

7.6.3 Airborne Sampling of Carbonyl Compounds

The performance audit for the aircraft sampling of carbonyl compounds will be similar to surface-based measurements. The main procedural difference is that the Tedlar bag will be filled with zero-air with addition of the standard carbonyl mixture.

7.7 Corrective Action

The systems and performance audits will be conducted prior to the field study in May and should be available in June, 1997. This schedule is probably optimistic based on experiences of past audit program of this type. Firm commitments from participating laboratories and sponsoring organizations will be required to minimize delays in disseminating the results of the audits that may lead to corrective actions.

The QA team will provide the results of the VOC performance audits and laboratory comparisons to participants as soon as they are available. It will be the obligation of each laboratory to examine the results, diagnose the cause for disagreements of their data with those reported by the majority of other laboratories, and take the necessary corrective actions.

7.8 Data Acquisition and Processing

Gas chromatographs and HPLC systems are connected to data acquisition systems that perform data acquisition, peak integration and identification, hardcopy output, post-run calculations, calibrations, and user interfacing. Acquired data are automatically stored on a hard disk. Typically the chromatographic information from the data acquisition system is post-processed to confirm peak identifications and to transfer the data to a spreadsheet or database format. In the case of carbonyl compounds, blank values are subtracted and blank uncertainties are combined with volume and analytical uncertainties.

7.9   Data Validation

The data validation process consists of procedures that identify deviations from measurement assumptions and procedures. Three levels of validation are applied which will result in the assignment to each measurement of one of the following ratings: 1) valid; 2) valid but suspect; or 3) invalid. Level 1 data validation normally takes place in the field or in the laboratory and consists of: 1) flagging samples when significant deviations from measurement assumptions have occurred; 2) verifying computer file entries against data sheets; 3) eliminating values for measurements which are known to be invalid because of instrument malfunctions; 4) adjustment of measurement values for quantifiable calibration or interference biases; 5) determining measurement precision by replicate analyses and by collection of field blanks and collocated samples.

Level 2 validation takes place after the data from various measurement methods have been assembled in a master database. Level 2 applies consistency tests based on known physical relationships between variables to the assembled data. These tests fall into three categories: detection of extreme values; consistency between redundant measurements and co-pollutants; and examination of temporal and spatial variations. The following are examples of level 2 validations for VOC measurements.

Detection of Extreme Values

- Derive summary statistics (mean, maximum, standard deviation) for all species and species groups, both for concentration and weight fractions. Sort the database by concentration and weight fraction of each species (including the less abundant species) and note any unusually high concentrations or fractions (any species) or unusually low concentrations or fractions of normally abundant species.

- Develop box-whisker plots of abundant species and species groups stratified by site, time of day.

- Stratify data by site and time of day and flag values above 5 ppbC for hydrocarbons and 2 ppbv for carbonyl compounds if the ratio of the absolute difference between sample and mean values to the standard deviation among values within the stratified group is greater than three (i.e., |value-mean|/sigma > 3). Examine patterns in occurrence of extreme points in time relative to wind direction, mixing height or some other physical variables, and determine if the unusual value is due to measurement error or a valid result of an environmental cause.

Consistency Checks

- Compare total nonmethane hydrocarbons derived from the sum of species measured by gas chromatography with flame ionization detection (TO-14 Method) and preconcentration direct Injection flame ionization detection (PDFID), TO-12 Method.

- Prepare scatter plots of NMOC and NMHC versus CO, benzene, toluene, and other abundant species; benzene versus toluene; propane versus n-butane and note outliers. For each site and sampling period, examine distributions of the following ratios: benzene/CO, methane/NMOG, olefins/NMOG, aromatics/NMOG, carbonyls/NMOG, CO/NO_X and $NMOG/NO_X$ ratios. We will apply appropriate range limits (e.g., differences of no greater than three standard deviation of all values for each site and period), and identify outliers).

Temporal and Spatial Variability

- Prepare time-series plots of abundant species and compare sample-to-sample, site-to-site, date-to-date, and sampling period-to-sampling period variations.

- Plot monthly mean diurnal variations by site and examine consistency of diurnal patterns with respect to patterns in emissions, atmospheric chemistry, and seasonal meteorological changes.

Level 3 validation is part of the subsequent data interpretation process. Receptor modeling, factor and other statistical analyses, and photochemical air quality simulation models are several examples. Unusual values are identified during the data interpretation process as: 1) extreme values; 2) values which would otherwise normally track the values of the other variables in a time series; and 3) values for observables which would normally follow a qualitatively predictable spatial or temporal pattern.

7.10 Data Archival

Data from the Air Pollution Control Districts are archived in AIRS format and are submitted to ARB and EPA. Data from the supplemental measurements will be archived in accordance with the format specified by the SCOS97-NARSTO Data Manager.